

## Hydrogenation Reactivity of Petrographic Composition of Coal

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### Introduction

With special regard to the characteristics of high pressure hydrogenation of the petrographic composition of coal, in the past reports by Bergius<sup>1)</sup>, Wright et al<sup>2)</sup>, Fisher et al<sup>3)</sup> are available, and more recently we have reports on the results of work by Given, Davis and Mitchell et al<sup>4)-7)</sup>. According to these reports, among the 3 maceral groups of coal, namely vitrinite, exinite and inertinite, it has been pointed out that the reactivity of vitrinite and exinite are high.

Among the coals produced in Australia, while there are rather large number of coals with a relatively high inertinite content, and whereas the main component of inertinite is semifusinite, generally the scarcity of fusinite is characteristic. While it is generally accepted that the hydrogenation reactivity of fusinite is low, no reports regarding semifusinite seen to be available.

In the present report we conducted liquefaction experiments by hydrogenation reaction on hand picked vitrinite concentrates and inertinite concentrates of Bayswater seam coal (N.S.W., Australia), and the respective features of liquefaction reaction were clarified and a comparative investigation was made between the two.

### Experimental

The samples used in the experiments were vitrinite concentrates and inertinite concentrates hand picked from Bayswater seam coal of high volatile bituminous rank. The petrographic, proximate and ultimate analyses of the hand-picked samples are given in Table 1. In the experiments we used a batch type autoclave with an inner volume of 500 cc as the hydrogenation apparatus. In the once experiment, we inserted 10 g of dry sample coal, 1 g of red mud catalyst, 0.1 g sulfur promoter together with 10 steel balls for agitation, and the hydrogenation reaction was conducted under an initial hydrogen pressure of 100 kg/cm<sup>2</sup> at reaction temperatures of 400°C and 450°C respectively and by changing the reaction time from 0-150 minutes. In the case where vehicle oil was used, we applied decrystallized anthracene oil.

Among the reaction products, the gas was dealt with gas chromatography and the composition thereof was measured. Regarding the liquid and solid products, using n-hexane, benzene were fractionated into oil-1(O<sub>1</sub>), oil-2(O<sub>2</sub>), asphaltene(A), and organic benzene insolubles (O.B.I). The conversion was calculated from total product(gas+O<sub>1</sub>+O<sub>2</sub>+A). In addition O.B.I. was subjected to extracting tests using pyridine. The details of the above are as seen in our previous report<sup>8)</sup>.

### Results and discussion

In Fig. 1 is shown the changes by reaction time of the yield of each fraction

of hydrogenation products of vitrinite and those of inertinite are shown in Fig. 2.

Even at a reaction temperature of 400°C the reaction of vitrinite proceeds and the conversion increases with the reaction time however the conversion of inertinite does not exceed 15% or thereabouts. However, in the case where vehicle oil is added to inertinite, even under identical reaction conditions the conversion increases markedly to 45% or thereabouts.

When this vehicle oil is used, this conversion is attained by the nominal reaction time zero. From the previous paper<sup>9</sup>), it may be considered that the coal hydrogenation reaction with vehicle oil proceeds by the chemical reaction controlling. Therefore, it may be understood that the initial stage reaction rate of inertinite is very fast. However, thereafter ever what the reaction time is increased, no increase in the conversion was recognized, and it is surmized that the portion which can react under certain given conditions is restricted. Whereas the equilibrium conversion is higher than 400°C a similar tendency is seen when the reaction temperature is 450°C. This point is that which differs from vitrinite in which a gradual increase is seen with the increase in reaction time. However, when the distribution of reaction products is viewed, the distribution of gas, oil and asphaltene in both cases is relatively similar.

Further, hydrogen consumption of both cases in hydrogenation is as shown in Table 2, it may be seen that in the case of inertinite approximately 2 fold values are seen. The molecular weight of the reaction products of both cases are as seen in Table 3. When the reaction temperature becomes 450°C, a relative fairly good coincidence is seen between the vitrinite and inertinite, however when the reaction temperature is 400°C, it may be noted that the reaction products from inertinite show higher values. The H-NMR spectra of oil-1 and oil-2 of inertinite at 400°C are shown in Fig. 3; as may be seen an approximately similar pattern is recognized. Similarly the H-NMR spectra of oil-1 of inertinite at 150 minutes, 400°C, and oil-1, oil-2 of vitrinite at 30 minutes, 400°C as shown in Fig. 4 show a similar pattern.

Thus from the above, it may be surmized that product from the liquefaction of the main parts of both sample coal have a relatively similar composition.

#### Conclusion

- 1) The reaction rate of vitrinite shows a gradual increase with the reaction time, however in the case of inertinite, the reaction does not proceed beyond a given value. This given value shows an increase with the rise in reaction temperature and the reaction rate is fast up till the time that this value is attained.
- 2) The hydrogen consumption is larger in inertinite.
- 3) It may be surmized that the liquefaction products from the main part of both sample coal have a relatively similar composition.

#### References

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Table 1 Petrographic, Proximate and Ultimate Analysis of Bayswater Seam Coal

Sample	Maceral analysis (%)					Proximate analysis (%)				Ultimate analysis (%)				
	Vitrinite	Exinite	Miorinite	Semi-fusinite	Fusinite	Moisture	Ash	Volatiles matter	Fixed carbon	C	H	N	S	O
Vitrinite concentrate	99	0.5	0.5	tr	tr	3.4	1.6	32.9	62.1	83.0	5.3	2.0	0.5	9.2
Inertinite concentrate	0.5	5	4	90	0.5	4.5	16.2	20.8	58.5	85.0	4.1	1.9	0.3	8.7

Table 2 Hydrogen consumption of vitrinite and inertinite hydrogenation

Sample	R.T °C	Rt min.	H <sub>2</sub> consumption	
			wt % of coal	wt % of coal/conversion
Vitrinite	400	0	0.75	6.1 × 10 <sup>-2</sup>
"	"	30	1.24	5.6 "
"	"	60	3.42	7.0 "
"	"	90	2.95	4.5 "
"	"	120	3.52	4.9 "
"	"	150	4.22	5.4 "
"	425	60	4.84	6.9 "
"	450	0	1.37	2.7 "
"	"	30	4.20	5.4 "
"	"	60	5.40	6.1 "
Inertinite	400	0	2.05	1.8 × 10 <sup>-1</sup>
"	"	30	2.64	1.6 "
"	"	60	1.39	1.4 "
"	"	150	2.95	2.5 "
"	410	60	1.30	1.3 "
"	425	60	2.80	1.4 "
"	435	60	2.23	0.6 "
"	450	0	1.38	1.1 "
"	"	30	1.67	4.9 "
"	"	60	5.05	0.9 "
"	"	90	4.72	0.9 "
"	"	120	4.99	0.9 "
"	"	150	5.86	1.0 "

Table 3 Molecular weight of inertinite and vitrinite hydrogenation product

Raw Sample	R.T °C	Rt min.	oil-1	Product oil-2	Asphaltene
Vitrinite	400	0	340	500	-
"	"	30	-	-	680
"	"	60	320	450	660
"	"	90	300	360	700
"	"	120	-	420	760
"	"	150	420	530	770
"	425	60	290	450	750
"	450	0	340	460	580
"	"	30	280	480	800
"	"	60	300	370	850
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Inertinite	400	0	490	460	470
"	"	30	470	500	520
"	"	60	420	530	530
"	"	150	400	580	-
"	410	60	440	550	630
"	425	60	340	440	580
"	435	60	-	370	620
"	450	0	370	630	590
"	"	30	350	420	590
"	"	60	340	510	830
"	"	90	350	370	650
"	"	120	350	440	690
"	"	150	320	420	690

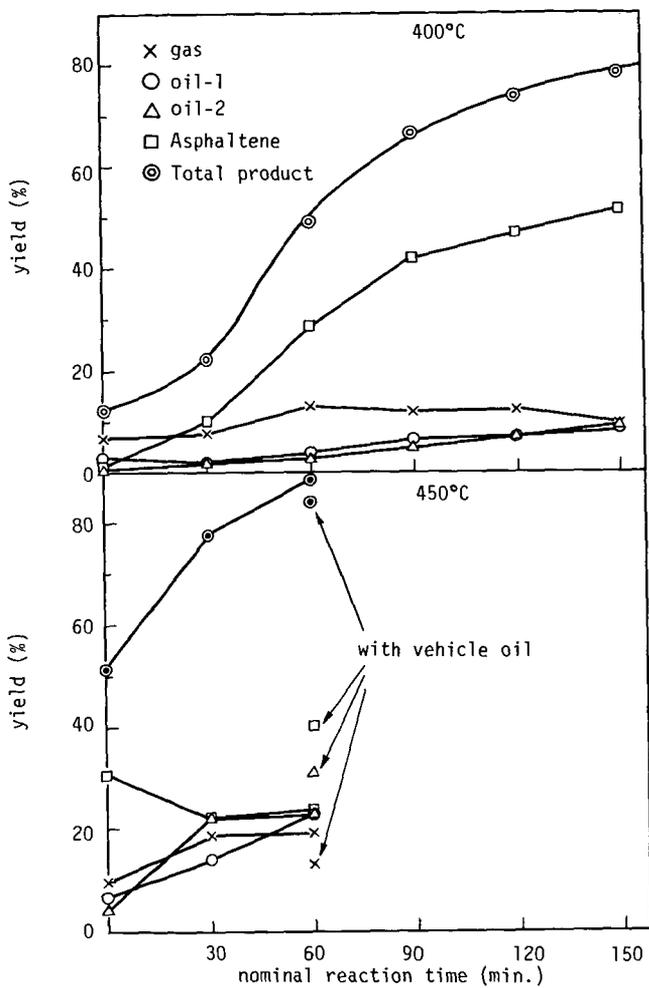


Fig. 1 Distribution of hydrogenation products from Bayswater vitrinite at 400°C, 450°C

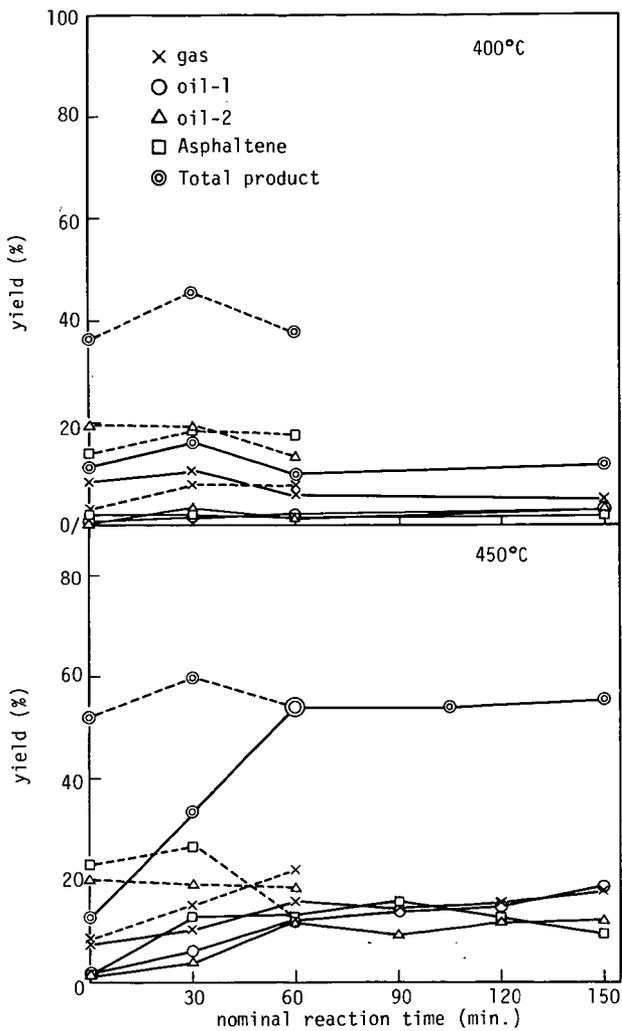


Fig. 2 Distribution of hydrogenation products from Bayswater inertinite at 400°C, 450°C

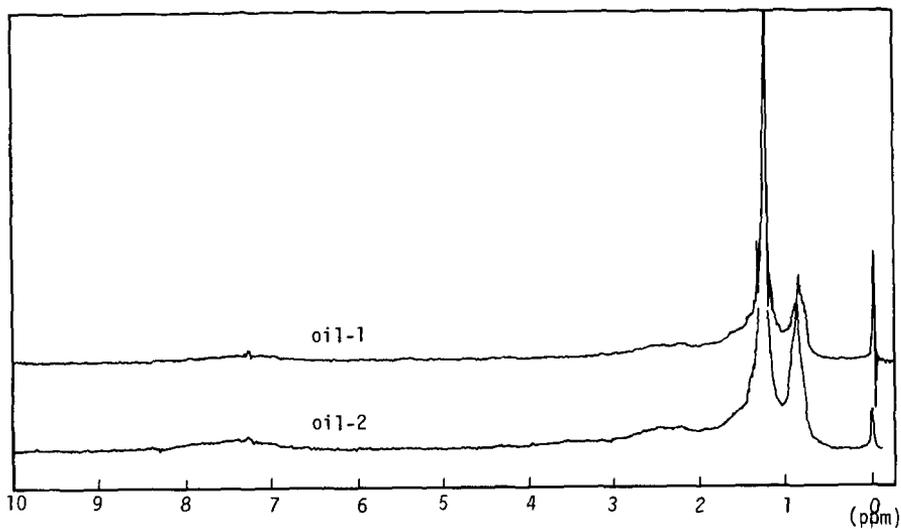


Fig. 3 H-NMR spectra of oils from inertinite hydrogenation at 400°C(Rt:30 min.)

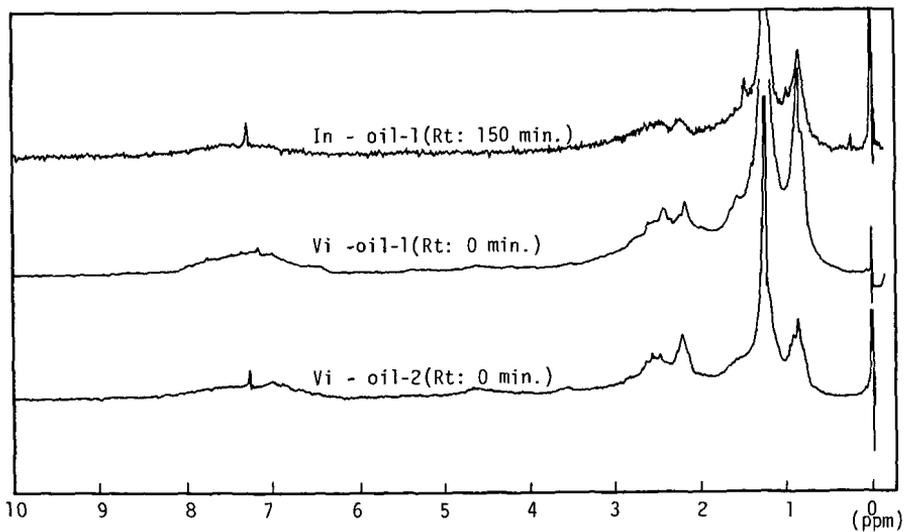


Fig. 4 H-NMR spectra of oils from inertinite and vitrinite hydrogenation at 400°C